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JC10 Rec'd PCT/PTO 19 DEC 2001

UNITED STATES PATENT APPLICATION TRANSMITTAL FORM

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COMMISSIONER FOR PATENTS
Washington, D.C. 20231
Attention: DO/EO/US

Docket No.: 308.7553USU

Dear Sir:

Transmitted herewith for filing is the patent application of

Applicant: Mika Martikainen
For: PROCESS FOR MAKING HIGH DENSITY AND
LARGE PARTICLE SIZE COBALT HYDROXIDE
OR COBALT MIXED HYDROXIDES AND A
PRODUCT MADE BY THIS PROCESS
International Application No.: PCT/FI00/00581
International Filing Date: 28 June 2000

ENTERING OF U.S. NATIONAL STAGE UNDER 35 U.S.C. §371

Transmitted herewith for filing are the following documents submitted under 37 C.F.R. §1.495(b) for the purpose of entering the national stage in the United States of America as an elected office. Enclosed are:

_____ Specification and Claims with Declaration;
XXXX Specification and Claims *without* Declaration;
XXXX 1 sheet of drawings;
XXXX Preliminary Amendment;
_____ An Assignment of the invention document to: _____,
including the \$40.00 recordation fee;
_____ The certified copy of a priority application;
XXXX Information Disclosure Statement with copies of patent(s) (Form -
PTO-1449);
_____ The undersigned attorney has verified that the application is
entitled to a Small Entity Status;

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XXXX Priority of application no. 991478, filed on 29 June 1999 in Finland; and International application no. PCT/FI00/00581 filed on 28 June 2000 in Finland;

XXXX Cover page of published PCT Publication No. WO 01/00532;

XXXX Copy of International Preliminary Examination dated 17 September 2001;

_____ Copy of PCT Demand Under Article 31;

XXXX Copy of International Search Report dated 26 October 2000;

XXXX Copy of Finnish Search Report dated 11 January 2000;

XXXX Copy of Written Opinion dated 15 June 2001;

XXXX Copy of Response to Written Opinion dated 07 August 2001;

_____ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) are transmitted herewith.

The Filing Fee is calculated below.

CLAIMS AS FILED				
(1) For	(2) Number Filed	(3) Number Extra	(4) Rate	(5) Basic Fee \$710/\$740//\$890/ \$1,040/\$100
Total Claims	10 - 20 =	0	x \$18.00	\$0
Independent Claims	1 - 3 =	0	x \$84.00	\$0
Multiple Dependent Claim Fee		0 x \$280.00 = \$0		
TOTAL FILING FEE		\$1,040.00		
1/2 FILING FEE FOR SMALL ENTITY		N/A		

XXXX Firm's check in the amount of \$ 1040.00 to cover the filing fee (\$1040) is enclosed.

XXXX The Commissioner is hereby authorized to charge any additional fees under 37 C.F.R. 1.16 and 1.17 which may be required with this communication or during the entire pendency of the application, or credit any overpayment, to **Deposit Account No. 01-0467**. A duplicate copy of this Form is enclosed.

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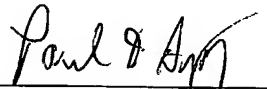
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December 19, 2001

Date of Signature



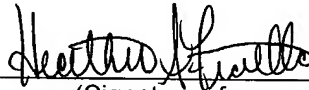
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CERTIFICATE OF EXPRESS MAILING

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Heather A. Fiorella

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(Signature of person mailing paper)

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#3/a

Applicants: Martikainen

Serial No.: Not yet assigned

Filed: Herewith

For: PROCESS FOR MAKING HIGH DENSITY AND LARGE PARTICLE
SIZE COBALT HYDROXIDE OR COBALT MIXED HYDROXIDES AND
A PRODUCT MADE BY THIS PROCESS

Examiner: Not yet assigned

Group: Not yet assigned

Docket No.: 308.7553USU

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, DC 20231

Sir:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please cancel claims 1 through 13.

Please add claims 14 through 23 as follows:

--14. A cobaltous hydroxide or alloy hydroxide formed of cobalt and one or more other metals, wherein the cobaltous hydroxide or alloy hydroxide has a density of about 0.5 to about

2.2 g/cm³, a particle size above about 1 µm, and a specific surface of about 0.5-20 m²/g, wherein the cobaltous hydroxide or alloy hydroxide is prepared by a reaction comprising the step of adding a complexing agent and hydroxide ion under alkaline conditions to an aqueous chloride solution of cobalt or to an aqueous chloride solution of an alloy of cobalt and one or more other metals to form metal hydroxide, wherein the complexing agent is selected so as to form an ammonium complex with the metal ion, the molar ratio of complexing agent to metal being about 0.5 to about 3 and the pH being adjusted in the range of 10 to 13.

15. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the particle size is about 1 µm to about 20 µm.

16. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the pH is in the range of 11.2 to 12.0.

17. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the one or more other metals is selected from the group consisting of: nickel, manganese, magnesium, aluminum, and alloys thereof.

18. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the chloride solution has a concentration in the range of 10 to 120 g/l, calculated on the total metal content.

19. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the complexing agent is ammonium sulphate or aqueous ammonia.

20. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the molar ratio of complexing agent to metal is about 1.5 to 2.

21. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the pH is adjusted with NaOH.

22. The cobaltous hydroxide or alloy hydroxide of claim 14, wherein the reaction is carried out at a temperature of about 40 to 90°C.

23. The cobaltous hydroxide or alloy hydroxide of claim 22, wherein the reaction is carried out at a temperature of about 70°C.--

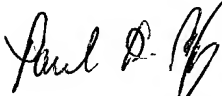
REMARKS

The claims have been amended by cancellation of claims 1 through 13 and the addition of claims 14 through 23.

Applicants respectfully request favorable consideration and passage of this application to allowance.

December 19, 2001

Respectfully submitted,



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Method for preparing cobaltous hydroxide with high density and large particle size or cobalt alloy hydroxide and product obtained with the method

5 The invention relates to a method for preparing cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal. The invention also relates to the product produced with this method.

10 Cobaltous hydroxide is used in many applications, for instance as an additive in chargeable NiMH and NiCd accumulators in the electronics industry. In addition, it is suitable for use as a precursor in the preparation of oxide products, such as LiCoO_2 and LiCoMO_2 (M stands for metal). Cobaltous hydroxide is also used as a catalyst or a precursor in catalyst production. A hydroxide product comprising any other metal in addition to cobalt, such as nickel, manganese, magnesium or aluminium, is also suitable for use for the purposes mentioned above.

15 There are many known methods for preparing cobaltous hydroxide in the field. The method of US patent 5,057,299 prepares cobaltous hydroxide by combining a cobaltous ion with a complexing agent, thus producing a water-soluble cobalt complex. Hydroxide ion is added to this, and the mixture is heated and kept in hydrothermal conditions until the cobaltous hydroxide precipitates. With the method of this US patent, the particle size increases at higher temperatures. Nonetheless, the
20 method of the patent allows the particle size to be controlled only in the range from approx. 0.05 to 0.5 μm by means of the temperature.

In applications of the accumulator industry, NiCd and NIMH accumulators are required to have good capacity. The capacity can be raised by using cobaltous hydroxide with maximum density as an additive in accumulators. In addition to this,
25 it is important that the cobaltous hydroxide used in the production of oxide products has a small specific surface and a high density. The purpose of the present invention is to provide a method for preparing cobaltous hydroxide particles with a large particle size or alloy hydroxide particles of cobalt and some other metal with a method that is easy to control. The purpose is to achieve cobaltous hydroxide
30 particles or alloy hydroxide particles of cobalt and some other metal with a particle size above 1 μm , preferably above 3 μm . This has been achieved according to the invention in the manner described in the accompanying claims.

Besides cobaltous hydroxide, the method in accordance with the invention can be used to prepare alloy hydroxides of cobalt and one or more other metals. The other

metals used may comprise for instance nickel, manganese, magnesium or aluminium, or alloys of these, depending on the purpose of use.

5 The starting material used in the method of the invention is an aqueous brine of cobalt or cobalt and alloy metals in the form of sulphate, nitrate or chloride. The concentration of the solution may vary in the range from 10 to 120 g/l calculated on the total metal content.

10 A complexing agent that forms an ammonium complex with the metal ion is added to this metal brine. The complexing agent may be ammonium sulphate, aqueous ammonia or any other ammonium ion source. In principle, the complexing agent may also be some other substance forming a complex with a metal, such as for instance EDTA. In the present invention, ammonium ion has nevertheless proved a good complexing agent owing to its economic price and good complexing characteristics. The molar ratio of the ammonium complexing agent to the metal introduced in the reactor is preferably about 0.5-3, most preferably about 1.5-2.0.

15 The reaction is performed under alkaline conditions and NaOH is preferably used for pH regulation. The preferred pH is in the range 10-13, most preferably the pH is in the range 11.2-12.0. The reaction is carried out at a temperature of about 40-90 °C, preferably at a temperature of about 70 °C. The method in accordance with the invention yields cobaltous hydroxide with a density of about 0.5-2.2 g/cm³, a particle size above approx. 1 µm, typically approx. 1-20 µm and a specific surface of approx. 0.5-20 m²/g.

20

The particles obtained with the method of the invention are plate-like cobaltous hydroxide particles in the shape of a hexagon. It was found in connection with the invention that chloride solutions yield thicker particles than sulphate-based solutions, with the other reaction conditions unaltered. Thicker particles are considered more suitable for instance for the preparation of lithium cobalt oxide.

25

In the method of the invention, the particle size of cobaltous hydroxide can be controlled by means of the molar ratio of the ammonium ion to the cobalt ion and of the pH used. Figure 1 shows the particle size variation as a function of pH with varied ratios NH₃ ion/Co. The figure shows that a pH increase reduces the particle size, and that the higher the ratio NH₃ ion/Co, the more notable the effect of the pH on the particle size.

30

The invention is illuminated below by means of examples. In examples 1-3 the method has been carried out as a comparison without complexing with ammonium

ions. Examples 4-6 illustrate the method of the invention, in which an ammonium complex with cobalt is formed. Example 7 exemplifies the method of the invention, in which nickel was used in addition to cobalt. The reaction temperature in the examples was 70 °C.

5 Comparative example 1

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into a first reactor. The pH was maintained constant in the range 11.8-12.0 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow, resulting in pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was 0.9 μm when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.5 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was 30 m^2/g .

Comparative example 2

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor. The pH was maintained constant in the range 11.6-11.8 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed Co(OH)_2 cake was dried.

The average particle size D50 of the dried Co(OH)_2 was 1.1 μm when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous Co(OH)_2 slurry). The density was 0.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was 29 m^2/g .

Comparative example 3

An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5.

The overflow from the second reactor was filtered and washed with water. The washed $\text{Co}(\text{OH})_2$ cake was dried.

- 5 The average particle size D50 of the dried $\text{Co}(\text{OH})_2$ was $1.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous $\text{Co}(\text{OH})_2$ slurry). The density was 0.6 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $35 \text{ m}^2/\text{g}$.

Example 4

- 10 An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonia. The pH was maintained constant in the range 11.8-12.0 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed $\text{Co}(\text{OH})_2$ cake was dried.

- 15 The average particle size D50 of the dried $\text{Co}(\text{OH})_2$ was $1.8 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous $\text{Co}(\text{OH})_2$ slurry). The density was 0.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $5.8 \text{ m}^2/\text{g}$.

Example 5

- 20 An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonium. The pH was maintained constant in the range 11.6-11.8 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain
25 pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed $\text{Co}(\text{OH})_2$ cake was dried.

- 30 The average particle size D50 of the dried $\text{Co}(\text{OH})_2$ was $3.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous $\text{Co}(\text{OH})_2$ slurry). The density was 1.2 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $2.6 \text{ m}^2/\text{g}$.

Example 6

5 An aqueous solution of CoCl_2 (30 g/l Co) was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio 2 metal/ammonium. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. The overflow from the second reactor was filtered and washed with water. The washed $\text{Co}(\text{OH})_2$ cake was dried.

10 The average particle size D50 of the dried $\text{Co}(\text{OH})_2$ was $7.4 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous $\text{Co}(\text{OH})_2$ slurry). The density was 1.7 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $1.8 \text{ m}^2/\text{g}$.

Example 7

15 An alloy brine was prepared which contained CoCl_2 and NiCl_2 solutions (30 g/l Co and 8g/l Ni). The solution was introduced continually into the first reactor, which contained an aqueous solution of ammonia with the molar ratio metal/ammonium being 2. The pH was maintained constant in the range 11.2-11.4 by adding sodium hydroxide solution. The overflow of the first reactor was conducted to the second reactor, where sodium hydroxide was added to the flow so as to obtain pH 13.5. 20 The overflow from the second reactor was filtered and washed with water. The washed $\text{Co}(\text{OH})_2$ cake was dried.

25 The chemical analysis indicated precipitation of alloy hydroxide. The average particle size D50 of the dried $\text{Co}_{0.8}\text{Ni}_{0.2}(\text{OH})_2$ was $6.9 \mu\text{m}$ when determined with a Malvern Mastersizer particle size analyser (the determination was performed with laser diffraction on an aqueous $\text{Co}(\text{OH})_2$ slurry). The density was 1.6 g/cm^3 (ASTM B527-93). The specific surface (BET ASTM D4567-86) was $3.2 \text{ m}^2/\text{g}$.

To facilitate the comparison, the table below shows the physical properties of the products exemplified above. The table also shows the crystal size of the products, which was measured with an X-ray diffraction meter.

Table 1

Example	Precipitated pH	Complexing agent	Average particle size (μm)	Density (g/cm^3)	Specific surface (m^2/g)	XRD (001) (nm)	XRD (101) (nm)
Comparative example 1	11.8-12.0	None	0.9	0.5	30	23	27
Comparative example 2	11.6-11.8	None	1.1	0.7	29	26	30
Comparative example 3	11.2-11.4	None	1.9	0.6	35	27	32
Example 4	11.8-12.0	NH_3 ion	1.8	0.7	5.8	50	49
Example 5	11.6-11.8	NH_3 ion	3.9	1.2	2.6	56	56
Example 6	11.2-11.4	NH_3 ion	7.4	1.7	1.8	61	64
Example 7	11.2-11.4	NH_3 ion	6.9	1.6	3.2	59	57

- The table shows that, with ammonium ion used as the complexing agent, the product had a larger particle size and higher density than without a complexing agent. As an exception from this, the product of example 4 had a particle size and a density approximately equal to those of the comparative examples. In fact, the specific surface and crystal size of this product also equalled the values of the products of examples 5-7.
- 10 A number of applications of the invention have been presented above. The invention is naturally not restricted to the examples above, its principle being variable within the scope of protection of the claims.

Claims

1. A method for preparing cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal, in which a complexing agent and hydroxide ion is added under alkaline conditions to an aqueous cobalt brine or an aqueous brine of an alloy of cobalt and some other metal in order to form metal hydroxide, characterised in that the complexing agent is selected so as to form an ammonium complex with the metal ion, the molar ratio of complexing agent to metal being approx. 0.5-3 and the pH being regulated in the range 10-13.
2. A method as defined in claim 1, characterised in that the pH is regulated in the range 11.2-12.0.
3. A method as defined in claim 1, characterised in that the brine of cobalt or of the alloy of cobalt and some other metal is in the form of sulphate, nitrate or chloride.
4. A method as defined in claim 1, characterised in that the brine concentration is in the range from 10 to 120 g/l calculated on the total metal content.
5. A method as defined in claim 1, characterised in that the complexing agent is ammonium sulphate or aqueous ammonia
6. A method as defined in claim 1, characterised in that the molar ratio of complexing agent to metal is approx. 1.5-2.
7. A method as defined in claim 1, characterised in that NaOH is used for pH regulation.
8. A method as defined in claim 1, characterised in that the reaction is carried out at a temperature of about 40-90 °C.
9. A method as defined in claim 8, characterised in that the reaction is carried out at a temperature of about 70 °C.
10. A method as defined in claim 1, characterised in that the other metals used are nickel, manganese, magnesium or aluminium, or alloys of these.
11. Cobaltous hydroxide or alloy hydroxide formed of cobalt and some other metal, characterised in having a density of about 0.5-2.2 g/cm³, a particle size

above about 1 μm , typically about 1-20 μm , and a specific surface of about 0.5-20 m^2/g .

12. Cobaltous hydroxide or alloy hydroxide formed of cobalt and some other metal, characterised in that the other metal is nickel, manganese, magnesium or aluminium, or an alloy of these.

13. The cobaltous hydroxide or alloy hydroxide of cobalt and some other metal as defined in claim 11 or 12, characterised in being prepared with a method of any of claims 1-10.

(57) Abstract

The invention relates to a method for preparing a cobaltous hydroxide with a high density and a large particle size or an alloy hydroxide of cobalt and some other metal, in which a complexing agent and hydroxide ion is added to an aqueous cobalt brine or an aqueous brine of cobalt and some other metal under alkaline conditions in order to form a metal hydroxide. In this method, the complexing agent is selected so as to form an ammonium complex with the metal ion. The molar ratio of complexing agent to metal is about 0.5-3, and the pH is regulated in the range 10-13.

1 / 1

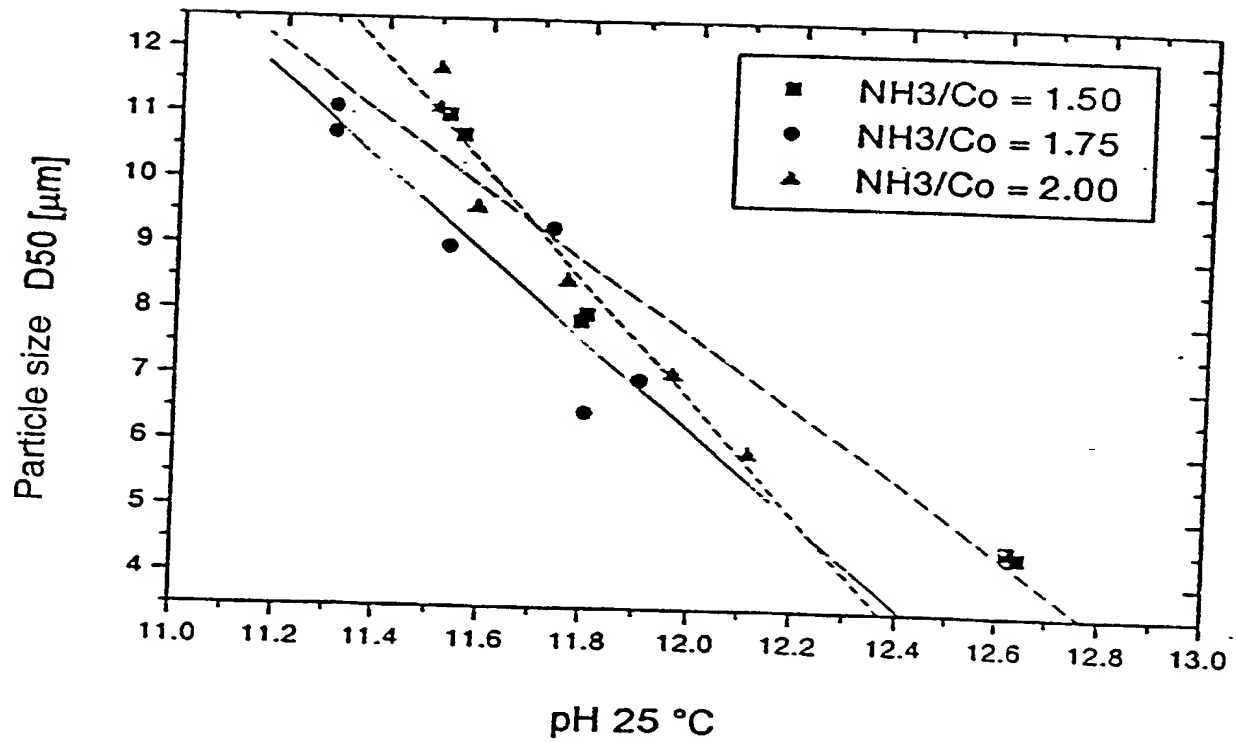


Figure 1

occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status - patent, pend., abandon.)
(Application Serial No.)	(Filing Date)	(Status - patent, pend., abandon.)
(Application Serial No.)	(Filing Date)	(Status - patent, pend., abandon.)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

NAMES	REGISTRATION NUMBERS
Paul D. Greeley	<u>31,019</u>
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature

Mika Martikainen

Date

25/03

, 2002